Notes

Titanium Dicarbollide Complexes. Molecular Structures of (η^5-$C_2B_9H_{11}$)(C_5Me_5)TiMe and (η^5-$C_2B_9H_{11}$)(η^5,η^1-$C_5Me_4CH_2$)Ti

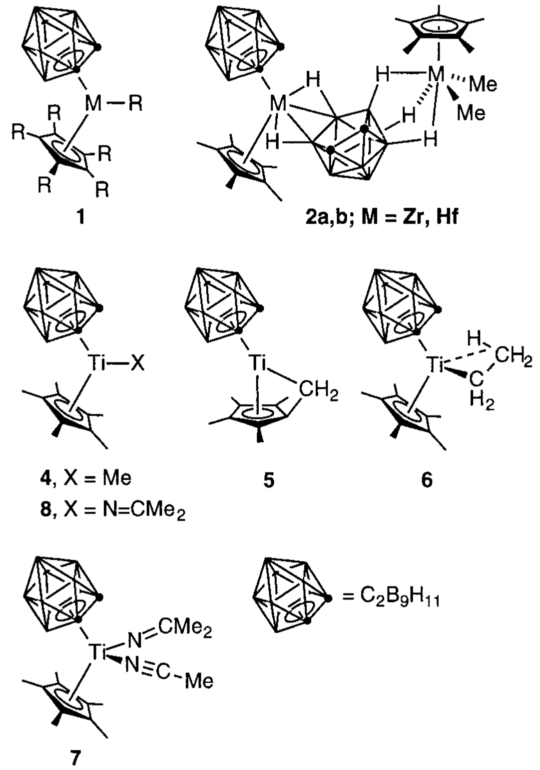
Xiaohong Bei,[†] Victor G. Young, Jr.,[‡] and Richard F. Jordan*,[†]

Department of Chemistry, The University of Chicago, 5735 S. Ellis Avenue,
Chicago, Illinois 60637, and Department of Chemistry, The University of Minnesota,
Minneapolis, Minnesota 55455

Received August 31, 2000

*Summary: X-ray structural studies establish that the titanium dicarbollide complexes (η^5-$C_2B_9H_{11}$)(C_5Me_5)-TiMe (**4**) and (η^5-$C_2B_9H_{11}$)(η^5,η^1-$C_5Me_4CH_2$)Ti (**5**) adopt bent metallocene structures. In **4** the metallocene units are linked into chains by weak intermolecular Ti- - -H−B interactions involving B−H units that are meta to Ti within the C_2B_9Ti cages. The fulvene ligand in **5** is bonded in a π-η^5,σ-η^1-fashion.*

Chart 1



Introduction

Group 4 metal dicarbollide complexes of general type (η^5-$C_2B_9H_{11}$)(η^5-C_5R_5)MR (**1**, Chart 1) are neutral analogues of the $(C_5R_5)_2MR^+$ active species in metallocene-catalyzed olefin polymerization and thus are of interest as model systems for studies of the influence of metal charge and ligand properties on the reactivity of olefin polymerization catalysts.[1,2] We have described the synthesis of Zr and Hf {(η^5-$C_2B_9H_{11}$)Cp*MMe}$_2$ compounds (**2a**,**b**; Cp* = C_5Me_5) and have shown that these species polymerize ethylene and oligomerize propylene by insertion/β-H elimination.[1,3] However, **2a**,**b** adopt dinuclear dicarbollide-bridged structures and insertion and σ-bond metathesis reactions of these species can lead to several other types of dinuclear and mononuclear structures.[4] For example, thermolysis of **2a**,**b** yields dinuclear μ-methylene species {(η^5-$C_2B_9H_{11}$)Cp*M}$_2$(μ-CH_2) (**3a**,**b**) via methane elimination.[1] The active catalyst species in the reactions of **2a**,**b** with olefins have not been identified.

To circumvent these complications, we investigated the chemistry of (η^5-$C_2B_9H_{11}$)Cp*TiMe (**4**), which is less likely to form dinuclear species due to the small Ti radius.[5] Compound **4** is prepared by the methane elimination reaction of Cp^*TiMe_3 and $C_2B_9H_{13}$ and decomposes at 23 °C with further methane elimination to yield the fulvene complex (η^5-$C_2B_9H_{11}$)($C_5Me_4CH_2$)-Ti (**5**). Compound **4** catalytically dimerizes ethylene to butene. In this reaction, the catalyst resting state is a β-H agostic ethyl species, (η^5-$C_2B_9H_{11}$)Cp*TiEt (**6**), and

---

[†] The University of Chicago.

[‡] The University of Minnesota.

(1) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455.

(2) For reviews covering Cp_2MR^+ chemistry, metallocene catalysis, and early metal carborane chemistry see: (a) Guram, A. S.; Jordan, R. F. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Lappert, M. F., Ed.; Pergamon/Elsevier: Oxford, 1995; Vol. 4, p 589. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (c) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081.

(3) (a) Crowther, D. J.; Jordan, R. F. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 121. (b) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *ACS Polymer Prepr.* **1992**, *33*, 1228. See also: (c) Bowen, D. E.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630. (d) Saccheo, S.; Gioia, G.; Grassi, A.; Bowen, D. E.; Jordan, R. F. *J. Mol. Catal. A* **1998**, *128*, 111.

(4) (a) Crowther, D. J.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1995**, *117*, 10403. (b) Yoshida, M.; Crowther, D. J.; Jordan, R. F. *Organometallics* **1997**, *16*, 1349. (c) Yoshida, M.; Jordan, R. F. *Organometallics* **1997**, *16*, 4508.

(5) (a) Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993. (b) Bei, X.; Kreuder, C.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 1085.

10.1021/om000759j CCC: $20.00
Publication on Web 12/06/2000

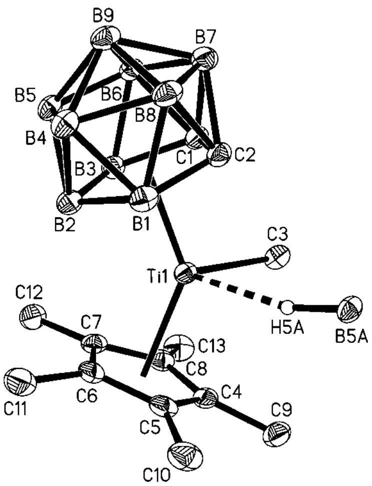


Figure 1. Structure of the bent metallocene unit of **4**. H5A and B5A are the bridging BH group of the adjacent metallocene unit within the polymeric chain. The other hydrogen atoms are omitted.

the (η^5-$C_2B_9H_{11}$)(Cp*)TiBu intermediate that is formed by ethylene insertion of **6** (not observed) undergoes β-H elimination much faster than ethylene insertion.[6] Compound **4** also reacts with acetonitrile to yield (η^5-$C_2B_9H_{11}$)Cp*Ti(N=CMe$_2$)(MeCN) (**7**) and (η^5-$C_2B_9H_{11}$)-Cp*Ti(N=CMe$_2$) (**8**), for which mononuclear structures were established by X-ray crystallography.[5a] However, one key issue that was left unresolved in this work is the question of whether **4**–**6** adopt mononuclear or dinuclear structures. We have now succeeded in crystallizing **4** and **5** and have determined their molecular structures by X-ray diffraction.[7]

Results and Discussion

The molecular structure of **4** is shown in Figures 1 and 2, and key bond distances and angles are summarized in Table 1. The structure consists of discrete (η^5-$C_2B_9H_{11}$)Cp*TiMe bent metallocene units (Figure 1) which are linked into chains by intermolecular Ti- - -H–B interactions involving the B(5)–H group which is meta to Ti within the C_2B_9Ti cage (Figure 2). The Ti–Cp* centroid and Ti–dicarbollide centroid distances (2.08, 1.96 Å) and the centroid–Ti–centroid angle (139.2°) are intermediate between the corresponding values for the four-coordinate complex **7** (2.09, 2.02 Å; 138.7°) and three-coordinate complex **8** (2.07, 1.91 Å; 144.6°), which is consistent with the presence of one weak donor ligand in **4** (i.e., the Ti- - -H–B interaction).[5a] The Ti- - -H–B interaction in **4** is reminiscent of the ion-pairing in [(C_5H_4Me)$_2$Zr(Me)][($CB_{11}H_{12}$)] (**9**), in which the carboranyl anion is linked to the Zr cation by a Zr- - -H–B bridge.[8] However, the Ti- - -HB distance (2.25(2) Å) and the Ti- - -H–B angle (165(2)°) for **4** are greater than the corresponding values for **9** (Zr- - -HB, 2.06 Å; Zr- - -H–B, 123°), which is consistent with a much weaker interaction in the former case as expected on the basis of charge considerations. The B–H$_{\text{bridge}}$ distance (1.16(2) Å) in **4** is slightly longer than the B–H$_{\text{terminal}}$ distances (range: 1.05(3)–1.11(3) Å). The Ti–Me group occupies a lateral coordination site of the bent metallocene, and the H$_{\text{bridge}}$–Ti–Me angle is 77.6°. However, NMR data establish that **4** has a C_s-symmetric structure in toluene-d_8 solution down to −80 °C, so the Ti- - -HB interactions must be labile on the NMR time scale. It is likely that **4** is dissociated into monomeric species in solution.[5a]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (η^5-$C_2B_9H_{11}$)Cp*TiMe (4)

Ti(1)–C(1)	2.493(2)	Ti(1)–C(4)	2.410(2)
Ti(1)–C(2)	2.382(2)	Ti(1)–C(5)	2.408(2)
Ti(1)–B(1)	2.332(3)	Ti(1)–C(6)	2.420(2)
Ti(1)–B(2)	2.450(3)	Ti(1)–C(7)	2.396(2)
Ti(1)–B(3)	2.475(3)	Ti(1)–C(8)	2.392(2)
Ti(1)–C(3)	2.160(2)	Ti(1)- - -H(5A)	2.25(2)
Ti(1)–CntA[a]	2.08	Ti(1)–CntB[b]	1.96
CntA–Ti–CntB	139.2	H(5A)–Ti–C(3)	77.6

[a] CntA = centroid of Cp*. [b] CntB = centroid of $C_2B_9H_{11}$ donor ring.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (η^5-$C_2B_9H_{11}$)($C_5Me_4CH_2$)Ti (5)

Ti(1)–C(1)	2.363(3)	Ti(1)–C(4)	2.306(3)
Ti(1)–C(2)	2.285(3)	Ti(1)–C(5)	2.446(3)
Ti(1)–B(1)	2.240(3)	Ti(1)–C(6)	2.378(3)
Ti(1)–B(2)	2.364(3)	Ti(1)–C(7)	2.197(3)
Ti(1)–B(3)	2.388(3)	Ti(1)–C(8)	2.294(3)
Ti(1)–C(3)	2.119(3)	C(3)–C(8)	1.439(4)
Ti(1)–CntA[a]	1.94	Ti(1)–CntB[b]	1.83
CntA–Ti–CntB	150.5	Ti(1)–C(8)–C(3)	64.5(2)

[a] CntA = centroid of fulvene C_5-ring. [b] CntB = centroid of $C_2B_9H_{11}$ donor ring.

The molecular structure of **5** is shown in Figure 3, and key metrical data are summarized in Table 2. Compound **5** has a bent metallocene structure with very short Ti–fulvene centroid and Ti–dicarbollide centroid distances (1.94, 1.83 Å) and a large centroid–Ti–centroid angle (150.5°), consistent with the low coordination number. The fulvene ligand is bonded to Ti in a π-η^5,σ-η^1-fashion. The coordination of the fulvene C_5 ring is unsymmetrical and features short Ti(1)–C(3) and Ti-

---

[6] In contrast, Cp_2Ti-based catalysts, in which Cp_2TiR^+ cations that are neutral analogues of **3** are presumed to be active species, polymerize ethylene to high molecular weight polymer but are unstable toward reduction to inactive Ti^{III} species. (a) Mallin, D. T.; Rausch, M. D.; Mintz, E. A.; Rheingold, A. L. *J. Organomet. Chem.* **1990**, *381*, 35. (b) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (c) Ewen, J. A. *Stud. Surf. Sci. Catal.* **1986**, *25*, 271. (d) Giannetti, E.; Nicoletti, G. M.; Mazzocchi, R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2117. (e) However, the discrete complexes [(C_5Me_5)$_2$Ti(Me)][BPh$_4$] and [(C_5Me_5)$_2$-Ti(Me)(tetrahydrothiophene)][BPh$_4$] are reported to be inactive with ethylene. See: Bochmann, M.; Jaggar, A. J. *J. Organomet. Chem.* **1992**, *424*, C5. (f) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H. *J. Mol. Catal.* **1990**, *62*, 277.

[7] For other group 4 metallocene complexes containing carborane ligands see: (a) Lo, F. Y.; Strouse, C. E.; Callahan, K. P.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 428. (b) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1976**, *15*, 2872. (c) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1984**, *13*, 599. (d) Siriwardane, U.; Zhang, H.; Hosmane, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 9637. (e) Hosmane, N. S.; Wang, Y.; Zhang, H.; Maguire, J. A.; Waldhör, E.; Kaim, W.; Binder, H.; Kremer, R. K. *Organometallics* **1994**, *13*, 4156. (f) Stockman, K. E.; Houseknecht, K. L.; Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1995**, *14*, 3014. (g) Thomas, C. J.; Jia, L.; Zhang, H.; Siriwardane, U.; Maguire, J. A.; Wang, Y.; Brooks, K. A.; Weiss, V. P.; Hosmane, N. S. *Organometallics* **1995**, *14*, 4, 1365. (h) Hosmane, N. S.; Wang, Y.; Zhang, H.; Lu, K.-J.; Maguire, J. A.; Gray, T. G.; Brooks, K. A.; Waldhör, E.; Kaim, W.; Kremer, R. K. *Organometallics* **1997**, *16*, 1365. (i) Mao, S. S. H.; Tilley, T. D.; Rheingold, A. L.; Hosmane, N. S. *J. Organomet. Chem.* **1997**, *533*, 257. (j) Hosmane, N. S.; Zhang, H.; Jia, L.; Colacot, T. J.; Maguire, J. A.; Wang, X.; Hosmane, S. N.; Brooks, K. A. *Organometallics* **1999**, *18*, 516.

[8] Crowther, D. J.; Borkowsky, S. L.; Swenson, D., Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897.

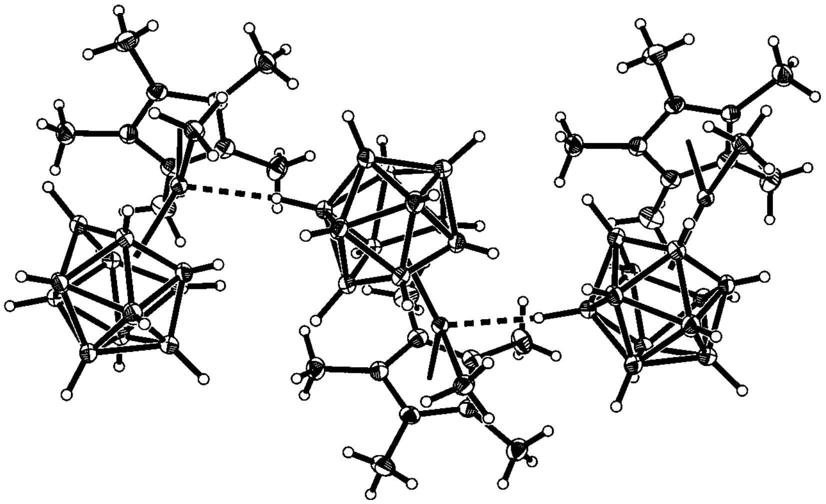


Figure 2. View of the polymeric chain structure of **4**.

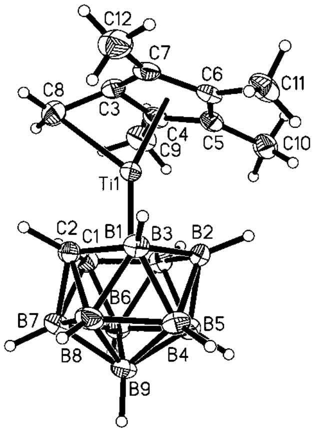


Figure 3. Molecular structure of **5**. Hydrogen atoms are omitted.

(1)−C(7) distances (2.119(3), 2.197(3) Å) and longer contacts to C(4), C(5), and C(6) (range 2.306(3)−2.446(3) Å). The methylene carbon C(8) is displaced by 39° out of the fulvene C_5-ring plane, and the Ti−C(8)−C(3) angle is highly acute (64.5(2)°). The Ti−C(8) distance (2.294 Å) is longer than a typical Ti^{IV}−C(sp^3) distance (cf. 2.160(3) Å in **4**), and the C(3)−C(8) bond is ca. 0.07 shorter than the fulvene C−Me bonds (av 1.51 Å). These features are ascribed to the strained environment at C(8) rather than to a significant contribution from a π-η^6 diene/exo-methylene resonance structure because the C−C distances within the fulvene C_5 ring are nearly equal (range: 1.413(4)−1.448(4) Å) and are typical for a C_5R_5 ligand (cf. 1.414(4)−1.426(3) Å for the Cp* ligand in **4**). The structure of the Ti−fulvene unit in **5** is very similar to that in the Ti^{III} complex Cp*($C_5Me_4CH_2$)Ti.[9]

These studies show that titanacarboranes **4** and **5** have simple bent metallocene structures in contrast to the more complex dinuclear structures found earlier for Zr and Hf complexes **2a**,**b**, **3a**,**b**, and derivatives thereof.[4] These results support our earlier proposal that the chemistry of the (η^5-$C_2B_9H_{11}$)(C_5Me_5)TiX system is dominated by mononuclear species.[5a]

Table 3. Crystallographic Data for (η^5-$C_2B_9H_{11}$)Cp*TiMe (4) and (η^5-$C_2B_9H_{11}$)($C_5Me_4CH_2$)Ti (5)

	4·(1.5toluene)	**5**
formula	$C_{23.5}H_{41}B_9Ti$	$C_{12}H_{25}B_9Ti$
cryst size (mm)	0.50 × 0.12 × 0.08	0.45 × 0.43 × 0.08
color/shape	red/needle	red/plate
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a (Å)	11.7222(5)	10.6112(2)
b (Å)	21.5332(9)	12.3861(1)
c (Å)	12.0058(5)	12.9354(1)
β (deg)	118.056(1)	
V (Å^3)	2674.4(2)	1700.12(4)
Z	4	4
μ (mm^{-1})	0.331	0.488
diffractometer	Siemens SMART CCD	Siemens SMART CCD
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
temp (K)	148(2)	173 (2)
θ range (deg)	1.89−25.07	2.28−24.97
data collected: *h; k; l*	−13,12; 0,25; 0,14	±12; 0,14; 0,15
no. of reflns	18 468	8563
no. of unique reflns	4717 (R_{int} = 0.0423)	2976 (R_{int} = 0.0324)
no. of obsd reflns	$I > 2\sigma(I)$, 3718	$I > 2\sigma(I)$, 2705
structure solution	direct methods	direct methods
refinement	FMLS on F^2	FMLS on F^2
abs corr	SADABS	SADABS
transmn range (%)	83−100	79−100
no. of data/restraints/params	4717/0/347	2976/0/203
R indices ($I > 2\sigma(I)$)^{a,b}	R1 = 0.0518, wR2 = 0.0964	R1 = 0.0408, wR2 = 0.0901
R indices (all data)^{a,b}	R1 = 0.0771, wR2 = 0.1053	R1 = 0.0483, wR2 = 0.0940

[a] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = q/\sigma^2(F_o^2) + (aP)^2 + bP$.

Experimental Section[10]

(η^5-$C_2B_9H_{11}$)Cp*TiMe (4). A toluene solution (5 mL) of $C_2B_9H_{13}$ (64 mg, 0.5 mmol) was added to a toluene solution (10 mL) of Cp*$TiMe_3$ (115 mg, 0.5 mmol) at 23 °C. The solution was maintained at 23 °C for 5 min and then cooled to −65 °C. Dark red needles formed after 2 days. The crystals were handled and mounted at low temperature (−65 to −78 °C), and X-ray data were collected at −125 °C to avoid thermal decomposition to **5**. Details of the X-ray analysis are sum-

---

[9] Fischer, J. M.; Piers, W. E.; Young, V. C., Jr. *Organometallics* **1996**, *15*, 2410.

[10] Characterization data for **3** and **4** are given in ref 5a.

marized in Table 3. **4** crystallizes with 1.5 equiv of toluene per asymmetric unit. One toluene is found on a center of inversion giving rise to the fractional content. Non-hydrogen atoms were refined anisotropically. The dicarbollide cage hydrogen atoms were refined positionally with riding, relative isotropic displacement parameters. The methyl hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

(η^5-$C_2B_9H_{11}$)($C_5Me_4CH_2$)Ti (5). A benzene-d_6 solution (0.4 mL) of (η^5-$C_2B_9H_{11}$)Cp*TiMe (**4**, 11 mg) was maintained at 23 °C for 1 day. Dark red crystals of **5** formed. Details of the X-ray analysis are summarized in Table 3. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters.

Acknowledgment. This work was supported by DOE Grant DE-FG02-88ER13935.

Supporting Information Available: Summaries of X-ray diffraction data collection, structure solution and refinement procedures; drawings showing molecular structures and atom labeling; tables of crystal and refinement data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, torsion angles, and hydrogen atom coordinates for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000759J